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(54) **INTERMITTENT ELECTROLYTIC PACKED BED SUPPRESSOR REGENERATION FOR ION CHROMATOGRAPHY**

ZWISCHENZEITLICHE REGENERIERUNG EINES ELEKTROLYTISCHEN SCHÜTTGUTBETTES FÜR IONENCHROMATOGRAPHIE

REGENERATION INTERMITTENTE DU SUPPRESSEUR D'UN LIT A GARNISSAGE ELECTROLYTIQUE, EN CHROMATOGRAPHIE IONIQUE

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(73) Proprietor: **DIONEX CORPORATION**
Sunnyvale California 94086 (US)

(72) Inventors:
- **SMALL, Hamish**
  Leland, MI 49654 (US)
- **RIVIELLO, John, M.**
  Santa Cruz, CA 95062 (US)
- **RABIN, Steven, B.**
  Mountain View, CA 94043 (US)

(74) Representative: **Allard, Susan Joyce et al**
BOULT WADE TENNANT,
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

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US-A- 3 920 397 **US-A- 5 423 965**

- **PATENT ABSTRACTS OF JAPAN vol. 002, no. 152 (C-031), 20 December 1978 & JP 53 116278 A (NIPPON PAINT CO LTD), 11 October 1978**
- **JOURNAL OF CHROMATOGRAPHY, Volume 640, Issued 1993, S. RABIN et al., "New Membrane-Based Suppressor Device for Suppressed Conductivity Detection In Ion Chromatography", pages 97-109.**

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Description

Background of the Invention

[0001] The present invention relates to method and apparatus using suppression of eluents for the analysis of anions or cations in ion chromatography.

[0002] Ion chromatography is a known technique for the analysis of ions which typically includes a chromatographic separation stage using an eluent containing an electrolyte, and an eluent suppression stage, followed by detection, typically by an electrical conductivity detector. In the chromatographic separation stage, ions of an injected sample are eluted through a separation column using an electrolyte as the eluent. In the suppression stage, electrical conductivity of the electrolyte is suppressed but not that of the separated ions so that the latter may be determined by a conductivity cell. This technique is described in detail in U.S. Pat. Nos. 3,897,213, 3,920,397, 3,925,019 and 3,926,559.

[0003] Suppression or stripping of the electrolyte is described in the above prior art references by an ion exchange resin bed commonly referred to as a packed bed suppressor (PBS). The PBS requires periodic regeneration by flushing with an acid or base solution.

[0004] While packed bed suppressors have proven useful in ion chromatography, there are a number of disadvantages of PBS. These disadvantages include a) periodic regeneration of the PBS which interrupts sample analysis, b) a loss of resolution due to band broadening in the PBS and c) changes in retention of certain analytes as a function of the degree of exhaustion of the PBS.

[0005] The volume of the PBS suppressors is generally large as to contain sufficient ion exchange resin so that the suppression reaction can be performed for a large number of analysis (e.g. 15 to 50) prior to regeneration. By making the volume and capacity of the suppressor sufficiently large, the need to regenerate is less frequent which permits a larger number of samples to be analyzed before the system must be disrupted to regenerate the suppressor. Regeneration typically requires placing the suppressor out of line of the analytical system and pumping a concentrated acid or base solution (regenerant) through the suppressor.

[0006] If the suppressor's volume is too large, the separation of the analytes achieved in the separator column is compromised due to re-mixing of the analytes in the void volume, resulting in lower resolution.. Thus, the suppressor volume is a compromise between regeneration frequency and chromatographic resolution.

[0007] The regeneration process typically requires 20-60 minutes, depending on the volume of the suppressor. A strong acid or base solution is first pumped through the PBS in order to convert the resin to the acid (H_3O^+) or base (OH^-) form. After this conversion, deionized water is pumped through the suppressor until any traces of the highly conductive acid or base regenerant have been removed. The PBS is then placed back in line with the analytical system and is allowed to equilibrate before sample analysis is performed.

[0008] A different form of a suppressor is described and published in U.S. Pat No. 4,474,664, in which a charged ion exchange membrane in the form of a fiber or sheet is used in place of the resin bed. The sample and eluent are passed on one side of the membrane with a flowing regenerant on the other side, the membrane partitioning the regenerant from the effluent of the chromatographic separation. The membrane passes ions of the same charge as the exchangeable ions of the membrane to convert the electrolyte of the eluent to weakly ionized form, followed by detection of the ions.

[0009] Another suppression system is disclosed in U. S. Pat. No. 4,459,357. There, the effluent from a chromatographic column is passed through an open flow channel defined by flat membranes on both sides of the channel. On the opposite sides of both membranes are open channels through which regenerant solution is passed. As with the fiber suppressor, the flat membranes pass ions of the same charge as the exchangeable ions of the membrane. An electric field is passed between electrodes on opposite sides of the effluent channel to increase the mobility of the ion exchange. One problem with this electrodialytic membrane suppressor system is that very high voltages (50-500 volts DC) are required. As the liquid stream becomes deionized, electrical resistance increases, resulting in substantial heat production. Such heat is detrimental to effective detection because it greatly increases noise and decreases sensitivity.

[0010] In U.S. Pat. No. 4,403,039, another form of electrodialytic suppressor is disclosed in which the ion exchange membranes are in the form of concentric tubes. One of the electrodes is at the center of the innermost tube. One problem with this form of suppressor is limited exchange capacity. Although the electrical field enhances ion mobility, the device is still dependent on diffusion of ions in the bulk solution to the membrane.

[0011] Another form of suppressor is described in U. S. Pat. No. 4,999,098. In this apparatus, the suppressor includes at least one regenerant compartment and one chromatographic effluent compartment separated by an ion exchange membrane sheet. The sheet allows transmembrane passage of ions of the same charge as its exchangeable ions. Ion exchange screens are used in the regenerant and effluent compartments. Flow from the effluent compartment is directed to a detector, such as an electrical conductivity detector, for detecting the resolved ionic species. The screens provide ion exchange sites and serve to provide site to site transfer paths across the effluent flow channel so that suppression capacity is no longer limited by diffusion of ions in the bulk solution to the membrane. A sandwich suppressor is also disclosed including a second membrane sheet opposite to the first membrane sheet and defining a second regenerant compartment. Spaced electrodes

are disclosed in communication with both regenerant chambers along the length of the suppressor. By applying an electrical potential across the electrodes, there is an increase in the suppression capacity of the device. The patent discloses a typical regenerant solution (acid or base) flowing in the regenerant flow channels and supplied from a regenerant delivery source. In a typical anion analysis system, sodium hydroxide is the electrolyte developing reagent and sulfuric acid is the regenerant. The patent also discloses the possibility of using water to replace the regenerant solution in the electrodialytic mode.

[0012] Another improvement in suppression is described in U.S. Pat. No. 5,248,426. This form of suppressor was introduced in 1992 by Dionex Corporation under the name "Self Regenerating Suppressor" (SRS). A direct current power controller generates an electric field across two platinum electrodes to electrolyze water in the regenerant channels. Functionalized ion-exchange screens are present in the regenerant chambers to facilitate electric current passage with permselective ion-exchange membrane defining the chromatography eluent chamber, as in the '098 patent. After detection, the chromatography effluent is recycled through the suppressor to form a flowing sump for electrolyte ion as well as providing the water for the electrolysis generating acid or base for suppression.

[0013] The history of ion chromatography suppression is summarized in Rabin, S. et al. *J. of Chromatog.* 640 (1993) 97-109, incorporated herein by reference.

[0014] WO 95/06246 relates to an ion chromatography apparatus and method which uses a frequently regenerated batch-type suppressor.

[0015] The present invention provides a method of anion or cation analysis by ion chromatography using periodic electrolytic chemical regeneration of a packed bed suppressor, said method comprising

(a) chromatographically separating ionic species in a first liquid sample to be detected in a water-containing eluent solution comprising electrolyte to form a first chromatography effluent including separated ionic species,

(b) flowing said first chromatography effluent through a first packed bed suppressor including suppressor ion exchange resin with exchangeable ions to convert said electrolyte to weakly ionized form during suppression, thereby depleting at least some of said exchangeable ions on said suppressor ion exchange resin,

(c) flowing first suppressor effluent including the separated ionic species from said first packed bed suppressor through a detector in which the separated ionic species are detected to form a detector effluent, and

(d) applying an electrical potential through said first packed resin bed suppressor while flowing an aqueous liquid stream therethrough to electrolyze water in said aqueous liquid stream and thereby regenerate the exchangeable ions on said first suppressor ion exchange resin, the application of said electrical potential being discontinued during steps (a), (b) and (c).

[0016] The present invention also provides an apparatus for analysis of ions in a liquid sample solution, said apparatus comprising

(a) a first reservoir for a water-containing eluent solution comprising electrolyte,

(b) chromatographic separating means in communication with said first reservoir for receiving eluent therefrom, said chromatographic separating means comprising a chromatographic separating medium adapted to separate ionic species of a sample eluted therethrough using said eluent solution,

(c) means for injecting a liquid sample into said chromatographic separation means,

(d) a first suppressor comprising an ion exchange resin bed in communication with said chromatographic separating means,

(e) a detector in communication with said first suppressor, and

(f) means for applying an electrical potential through said ion exchange resin bed of said first suppressor, whereby, in use, water in a flowing aqueous stream is electrolysed and said ion exchange resin of said first suppressor is regenerated.

<u>Summary of the Invention</u>

[0017] The present invention relates to ion chromatography using electrochemical regeneration of a packed bed suppressor. Method and apparatus are provided using electrolytic chemical regeneration of a packed bed suppressor containing ion exchange resin. Ion chromatography is performed in a conventional manner by chromatographic separation, chemical suppression in a packed bed and detection. Thereafter, and before a second run, an electrical potential is passed through the packed bed suppressor while flowing an aqueous stream through it to electrolyze water in the stream and thereby create hydronium or hydroxide ions to regenerate the ion exchange resin. The packed bed suppressor with capacity sufficient for several analyses, has electrodes embedded in the resin, which permits electrochemical regeneration. Electrochemical regeneration is performed after one analysis, or after many analyses, depending on the capacity of the packed bed suppressor. In one embodiment, the aqueous liquid stream is the eluent. In another embodiment, the aqueous liquid stream is an independent water source, preferably deionized water. In that instance, appropriate valving is provided so that after a run, the deionized water is passed through the bed and electrolyte bypasses the bed, while the electrical potential is being applied to

regenerate the resin.

[0018] In a further embodiment, a second ion exchange resin bed is used with suitable valving to pass liquid streams through the system. In one alternative of this system, a second sample in an eluent stream is chromatographically separated, typically on a chromatographic column using an eluent. The eluent and separated second sample flow through a second packed bed suppressor including ion exchange resin to convert the electrolyte to weakly ionized form. Then, the separated sample ionic species in the suppressor effluent are detected in the detector. The effluent then flows through the first packed bed suppressor, forming the aqueous liquid stream required for regeneration and an electrical potential is applied and regeneration of the first packed bed suppressor is accomplished. The second suppressor may be similarly regenerated by positioning it after the detection cell and flowing through the detector effluent of the first sample and applying an electrical potential.

[0019] In another embodiment, the second suppressor is used solely as a flow-through polishing unit, not as a suppressor prior to detection. Instead, an eluent solution containing electrolyte flows through the polishing unit to convert the electrolyte into weakly ionized form and form a polished liquid effluent which flows through the first packed bed suppressor to supply the water source for electrolysis. The polishing unit is regenerated electrolyzing a stream of the first sample effluent from the detector.

[0020] Apparatus is provided to perform the above packed bed suppressor methods. Such apparatus includes a suppressor with an ion exchange resin bed and means for applying an electrical potential to electrolyze water in a flowing stream and regenerate suppressor ion exchange resin after use to suppress the electrolyte in the eluent stream.

[0021] One apparatus uses two packed bed suppressors with appropriate valving. In one valving embodiment, in a first valve position, a first sample is suppressed on a first suppressor and flows through the detector forming an aqueous liquid stream for regenerating the second suppressor while applying an electric field. In the second position, the flow is reversed as are the functions of the two suppressors. The electrical potential is applied only to that suppressor which is not in the flow system upstream of the detector.

[0022] In the polishing system, only one ion exchange packed bed is used as a suppressor while the other one is dedicated to providing a polished liquid for regeneration of the suppressor. The valving is substantially the same as the two-suppressor system.

Brief Description of the Drawings

[0023] Figures 1 and 2 are schematic views of two different systems according to the present invention using a single packed bed electrolytic chemical suppressor.

[0024] Figures 3 and 3a are embodiments of an electrolytic chemical packed bed suppressor according to the invention in cross-section and expanded partially broken away views.

[0025] Figures 4 and 4a are side view, partial cross-section and a cross-sectional view along the line A-A, of another electrolytic chemical packed bed suppressor.

[0026] Figure 5 is a cross-sectional view of another electrolytic chemical suppressor.

[0027] Figure 6 is a schematic view of a system according to the invention using two ion exchange packed beds, one used as a suppressor and the other as either a suppressor or polishing unit.

[0028] Figures 7 and 8 are chromatograms illustrating the present invention.

Detailed Description of the Preferred Embodiments

[0029] The system of the present invention is useful for determining a large number of ionic species so long as the species to be determined are solely anions or solely cations. A suitable sample includes surface waters, and other liquids such as industrial chemical wastes, body fluids, beverages such as fruits and wines and drinking water. When the term "ionic species" is used herein, it includes species in ionic form and components of molecules which are ionizable under the conditions of the present system.

[0030] The purpose of the suppressor stage is to reduce the conductivity, and hence noise, of the analysis stream background while enhancing the conductivity of the analytes (i.e., increasing the signal/noise ratio), while maintaining chromatographic efficiency. Thus, the following parameters are important to the performance of the suppressor: (1) capacity of the suppressor, measured as µEq/mL of the suppressor resin; (2) the volume of the suppressor; (3) the ratio of the i.d. to the length of the suppressor; and (4) background conductivity measured as µS/cm for each device.

[0031] The present invention relates to the intermittent use of the electric field during electrochemical suppression to minimize noise during detection of the ionic species. Specifically, it has been found that the suppressor can be regenerated to a sufficient extent to convert the chromatography electrolyte to a weakly dissociated form so that detection can be performed in the absence of the electric field. When used in this configuration, the requirement for chemical regenerants is eliminated, the assembly does not require the use of a membrane to provide uninterrupted use, the absence of a membrane allows a higher tolerance to system backpressure and reduces manufacturing costs, and, finally, this configuration reduces system noise because of the absence of an applied electrical field during detection. As used herein, the term intermittent electrochemical suppression will refer to this type of system.

[0032] It is preferable for electrolytic chemical packed bed regeneration to provide direct contact of the elec-

trodes with the ion exchange resin bed itself. For anion analysis using sodium hydroxide eluent, the cation exchange resin bed is regenerated to the hydronium ion form by formation of hydronium ions at the anode, which migrate toward the cathode, displacing sodium ions from the ion exchange sites. Sodium ions associate with hydroxide ions generated at the cathode and are eluted from the suppressor as sodium hydroxide. Current is conducted between the electrodes by movement of ions along ion exchange sites in the ion exchange material in the bed. After regeneration, the current is discontinued, and eluent is pumped through the bed to remove remaining gas bubbles. Then, the ionic species in a new sample solution are separated in the chromatography column, flow through the suppressor, and are detected.

[0033] Referring to Figure 1, one form of an ion chromatography system is illustrated using a single packed bed suppressor. The system includes analytical pump 150 connected by tubing 152 to sample injection valve 154 which in turn is connected by tubing 156 to chromatographic means typically in the form of a chromatographic column 158 filled with chromatographic resin. The effluent from chromatographic column 158 flows through tubing 160 to a packed ion exchange resin bed suppressor 162. Electrodes, in a form to be described below, are spaced apart in the suppressor with the ion exchange resin disposed between them. The electrodes are connected to a direct current power supply 164 by leads 165a and 165b. The configuration is such that with an aqueous stream in the suppressor and the application of power, water in the aqueous stream is electrolyzed to form a source of hydronium ion or hydroxide ion to regenerate the ion exchange resin. The suppressor effluent is directed through tubing 167 to a suitable detector and then to waste. A preferred detector is a conductivity detector 166 with the chromatography effluent flowing through the conductivity cell 168 of detector 166.

[0034] The suppressor 162 generates hydronium ions (and oxygen gas) at the anode (positive) electrode and hydroxide ions (and hydrogen gas) at the cathode (negative) electrode. In the first stage of operation, the power supply 164 is turned off. Thus, the system operates in the manner of a standard ion chromatography system. That is, a water-containing eluent solution including electrolyte is directed from pump 150 and through tubing 152. Sample is injected through sample injection valve 154, and is directed by tubing 156 into chromatographic column 158 to form a first chromatography effluent including separated ionic species of the sample.

[0035] For simplicity of description, the system will be described with respect to the analysis of anions using an eluent solution including sodium hydroxide as the electrolyte.

[0036] The chromatography effluent is directed in tubing 160 to suppressor 162. The suppressor includes cation exchange resin with exchangeable hydronium ions. The sodium ions of the electrolyte displace the hydronium ions on the column. The displaced hydronium ions combine with the hydroxide ions of the sodium hydroxide to form water. In this conventional process, the electrolyte is thus converted to weakly ionized form to accomplish suppression. During this process, the exchangeable hydrogen ions are depleted and replaced with sodium ions. Thereafter, the effluent from the suppressor is directed through conductivity cell 168 in which the separated anions are detected and from there to waste.

[0037] After completion of the analytical run (i.e., after chromatographic separation, suppression and detection), an electrical potential is applied through the resin in the packed bed suppressor while flowing an aqueous liquid stream to electrolyze water in the stream. Hydronium ions generated at the anode displace the sodium ions which associate with the hydroxide ions for passage to waste, in this instance through the conductivity cell.

[0038] Typical conditions for regeneration include current applied at a voltage ot 3 VDC to 50 VDC and preferably 5 VDC to 15 VDC and a current of 20 mA to 1000 mA and preferably 100 mA to 500 mA for a short period of time, suitably up to about 1 to 10 minutes and preferably on the order of 1 to 5 minutes while the aqueous liquid stream is flowing (e.g. at a rate of 1 mL/min) through the suppressor to provide the source of hydronium ions. In one embodiment, the source of hydronium ion is the eluent from reservoir 150 without any sample. Since the eluent includes sodium hydroxide, the current applied must produce sufficient hydronium ions to shitt the equilibrium toward the hydrogen ion form of the ion exchange resin in the suppressor.

[0039] After regeneration, the power supply 164 is discontinued and the aqueous liquid stream permitted to flow through the suppressor for sufficient time for equilibration, typically 1 to 5 minutes. This allows generated gas bubbles to sweep out of the bed and the settling of the conductivity cell and the baseline. Thereafter, a new sample is injected for subsequent detection. Since the eluent contains sodium ions, removal efficiency of sodium ions from the ion exchange sites is significantly reduced during regeneration. The sodium ions compete with the hydronium ions that are generated at the anode which can make it difficult to remove sodium ions. In certain instances, this can result in peak area variation as time proceeds as well as incomplete suppression of the analyte.

[0040] To overcome the foregoing potential problem, a source of water, preferably deionized water, may be directed through the suppressor during regeneration. Figure 2 illustrates a system for supplying deionized water to the suppressor during regeneration. Similar parts will be designated with similar numbers for Figures 1 and 2. Three-way slider valves 170 and 172 may be used for the proper shifting between the flow of deionized water and eluent. Deionized water is supplied by reservoir 176 under control of pressurized gas from source 178 through line 180 to valve 172.

[0041] Figure 2 illustrates the analytical run setting for valves 170 and 172. Specifically, the chromatography effluent from column 158 passes through tubing 160 to valve 170 through suppressor 162, valve 172, tubing 167 conductivity cell 168, and to waste. After completion of the run, the settings of valves 170 and 172 are reversed so that the deionized water in tank 176 passes through line 180, valve 172, suppressor 162, valve 170 and to waste. In this particular embodiment, the flow through the suppressor is reversed for suppression and regeneration. Other valving arrangements may be employed including one in which the flow is in the same direction so long as the deionized water and eluent are independently directed through the suppressor.

[0042] By use of deionized water, more complete regeneration can be accomplished in a shorter time and with a lower voltage current supply. For example, a suitable time for regeneration is on the order of 0.5 min to 5 min using a flowrate of 1 mL/min, a voltage of about 5 VDC to about 15 VDC, and a current of about 100 mA to 1000 mA.

[0043] Many different forms of electrolytic chemical suppressors may be employed in accordance with the present invention. High capacity (e.g., 2 to 10 mEq/g) resin conventionally used for ion chromatography suppressors is packed into a column. The operation of the column as a suppressor and its configuration can be similar to that of a conventional packed bed suppressor such as set forth in the aforementioned U.S. patents (3,897,213; 3,920,397; 3,925,019; and 3,926,559). An important feature of the suppressor is the use of means for applying an electrical potential across the ion exchange resin. Any number of configurations may be employed so long as the potential is applied to a significant part of the resin for efficient regeneration. In that regard, the anode and cathode should be spaced apart with the majority of the ion exchange resin disposed therebetween.

[0044] One embodiment of a suitable suppressor is illustrated in Figure 3. The flow-through housing (suitably in cylindrical cross-section) includes a body 200 with a central bore 202, screw-threaded top and bottom end caps 204 and 206, and top and bottom flow-through bed supports 208 and 210, respectively, at opposite ends of bore 202. A DC power supply 214 is connected to a cathode 216 and an anode 218. In this instance, the anode is formed into a helical spiral which extends along the length of bore 202. Cathode 216 coaxially projects in a generally straight line along the axis of the circular bore. The cathode and anode are suitably formed of platinum. High capacity ion exchange resin 220 is filled into bore 202 with cathode 216 and anode 218 in place. Above the top of the ion exchange resin bed and the electrodes is a small bed of neutral resin (e.g. formed of crosslinked polystyrene) or other porous neutral packing material. It serves the function of taking up the excess volume between the liquid connection to the suppressor column and the electrode which would otherwise be a source of band dispersion. Bed supports 208 and 210 are positioned and end caps 204 and 206 are screwed into a secured position. As is conventional, end caps include screw-threaded ports for connection to the inlet and outlet tubing.

[0045] Figure 3a illustrates an exploded view partially broken away of the configuration of anode and cathode in contact in the ion exchange resin bed.

[0046] Another embodiment of suitable electrolytic chemical suppressor is illustrated in Figure 4. Like parts will be designated with like numbers for Figures 3 and 4. In this instance, the DC power supply is connected to spaced cathode 216 and anode 218 separated by nonconducting spacers 224 and projecting from the top to the bottom of the suppressor along the ion exchange resin in direct contact with the resin. This is best illustrated in Figures 4a, a cross-sectional view along the line AA of Figure 4. The facing generally C-shaped cathode 216 and anode 218 project substantially along the entire length of ion exchange resin 220 in bore 202. At the top and bottom of the ion exchange resin bed are small beds of neutral polymeric resin 230 and 232, respectively. The reason for this neutral polymeric resin is the same as with respect to the embodiment of Figure 3 namely to take up excess volume and prevent peak dispersion.

[0047] Another embodiment of a suitable electrolytic chemical suppressor is illustrated in Figure 5. Like parts will be designated with like numbers to that of Figure 3. The main differences among the embodiments of Figures 3, 4, and 5 are the location, configuration and disposition of the anode and cathode. In Figure 5, the anode and cathode are at the top and bottom of the ion exchange resin beds. The anode and cathode are formed, for example, from a screen mesh or porous disc of platinum so as to allow liquid flow through the electrode and are placed directly on the top and bottom of the resin bed in direct contact with the resin.

[0048] In the case of screen mesh, a disc of porous polyethylene is also used outside the electrode as a resin bed support to hold the resin on the column. The cross section of the suppressor bed in this embodiment need not be circular. Square and rectangular cross sections with appropriate geometry electrodes placed at opposite ends of the resin bed are other embodiments of this design.

[0049] The embodiment of Figure 5 can have certain advantages. Since the electrodes are placed at the entry and exit ports of the column, this design efficiently removes sodium ions from the ion exchange sites because the suppressor generates hydronium ion at the entry in the flow direction, which allows these ions to displace sodium ions on the bed. Sodium ions can then exit the suppressor by association with hydroxide ions so they are generated at the exit port.

[0050] However, by placing the electrodes at the opposite ends of the ion exchange resin beds, flow preferably is counter-current to the flow of column effluent be-

cause it is best to generate the suppression ions (and thus conversion of the ion exchange sites) at the outlet end so that the bed is substantially regenerated for analysis. This prevents the counter-ions to the analyte from converting to the hydronium ion when entering the bed and then converting again to the sodium form upon exiting.

[0051] Referring to Figure 6, a form of the invention is illustrated which includes two electrolytic packed bed units. In one instance, only one of the ion exchange packed beds is used as a suppressor and the other one is used as a polishing unit. In the other system, both ion exchange packed beds are used as suppressors so that analyte is analyzed in one of the suppressors while the other one is being regenerated and then the system can be reversed. The setup of Figure 6 can be employed for either mode of operation.

[0052] Referring to Figure 6, an analytical pump 250 is connected by tubing 252 to sample injection valve 254, tubing 256 to analytical column 258, and then via tubing 260 to valve 262. One port of valve 262 is connected by tubing 264 to one end of suppressor 266. The other end of suppressor 266 is connected by tubing 268 to valve 270. A DC power supply 272 is connected to suppressor 266 in the manner set forth above. Valve 270 also includes a port connected by tubing 274 to suppressor 276 which, in turn, is also coupled to valve 262 by tubing 290 and to DC power supply 272, also as set forth above. Valve 262 includes a third port connected by line 280 to waste.

[0053] Valve 270 includes one port connected to tubing 268; and another port connected by tubing 282 to conductivity cell 284 of conductivity detector 286. Conductivity cell 284 is, in turn, connected by line 288 to another port of valve 270. Valve 270 includes another port connected by tubing 2.74 to one end of suppressor 276.

[0054] Referring to Figure 6 operation of a system in which both packed beds 266 and 276 are used for suppression is as follows. A sodium chloride analyte is eluted with a sodium hydroxide eluent or any other suitable eluent (e.g., sodium carbonate/bicarbonate). In the analytical stage, analytical pump 250 carries the eluent through line 252 and sample injected through valve 254 is carried in tubing 256 through chromatographic column 258 where the ionic species are separated. The effluent from column 258 is directed through tubing 260 to valve 262 and then through tubing 290 to previously regenerated suppressor 276 (with power from source 278 off). The effluent from suppressor 276 is directed through tubing 274 to valve 270, tubing 282 to conductivity cell 284 where the ionic species are detected. The effluent from conductivity cell 284 typically a weak acid (e.g. in water or carbonic acid), is directed in tubing 288 back through valve 270 through tubing 268 to suppressor 266 with the power supply 272 turned on. In this stage, the ion exchange resin in suppressor 266 is regenerated and the flow of effluent from this suppressor, including the electrolyte (e.g. sodium hydroxide), flows through tubing 264 back through valve 262 and through tubing 280 to waste.

[0055] After completion of an analytical run (including separation, suppression and detection) and adequate regeneration of suppressor 266 from a previous analytical run, valves 262 and 270 are reset so that suppressor 266 is on-line for suppression prior to detection and suppressor 276 is regenerated. With a new setting of the valves, the flow proceeds as follows. A new sample is injected through valve 254 and is carried by the eluent from analytical pump 250 through tubing 256, chromatographic column 258, valve 262 and through suppressor 266. During this time, DC power supply 272 is in the off position. After suppression of the eluent, the suppressor effluent flows through tubing 268, valve 270 to conductivity cell 284 in which the ionic species of the second sample are detected. The conductivity cell effluent flows in tubing 288 back to valve 270 and through tubing 274 and then through suppressor 276. In this instance, the conductivity cell effluent serves as the aqueous liquid stream supplying water for electrolysis by the application of current from DC power supply 278 to regenerate the ion exchange resin in suppressor 276. The effluent from suppressor 276 flows through tubing 290 valve 262 and to waste.

[0056] In the above system, one suppressor is functional to suppress eluent electrolyte after separation and prior to detection, with no power applied, while the other suppressor is off-line and being regenerated with power applied. Then the system is reversed.

[0057] Valve means in the form of valves 262 and 270 have first and second valve positions. In the first valve position liquid flows from the eluent reservoir through analytical pump 250, chromatographic separation column 258, suppressor 276, conductivity cell 284 to suppressor 266. In the second valve position, the eluent flows through analytical pump 250, sample injection valve 254, suppressor 266, detector 286 and suppressor 276. In the first valve position the ions in the sample solution are separated in column 258 and carried in the eluent through suppressor 276 in which the electrolyte is converted to weakly ionized form during suppression, and through conductivity cell 284 in which the ions are detected and through suppressor 266. In the second valve position, the eluent solution flows through suppressor 266 and then through suppressor 276.

[0058] In another embodiment, the suppressor 266 is used solely as a polishing column to deliver water with low ion concentration to the other suppressor for effective suppression. An advantage of this system is that only a single bed is used for analysis. This eliminates possible changes in peak responses due to differences in geometry which cause differences in dispersion in each suppressor. This may not be significant if the beds can be well matched. One disadvantage of this polishing technique compared to the foregoing polishing technique is that it takes longer for the full run including re-

generation.

[0059] The polishing system operates in a similar manner. In the first valve setting described above, the system operates identically for either the dual suppressor system or the suppressor/polishing unit system. In particular, the above description applies in which suppressor 276 is on-line as a suppressor after separation and before detection while suppressor 266 is being regenerated. The second valve setting is also the same, with the principal difference that no sample is injected during this cycle. Instead, in the second valve setting, suppressor 276 is regenerated and no readings are taken by conductivity detector 286. Thus, as in the above second valve setting, power supply 278 is on to regenerate suppressor 276 and power supply 272 is off with no analytical function being performed by suppressor 266. Instead, it serves solely as a polish column to supply water of low ionic content to suppressor 276 during the regeneration mode.

[0060] In either the dual suppressor mode or suppressor/polisher mode, suppression is performed in accordance with the conditions well known in the art for packed bed suppression for example as illustrated U.S. Pat. Nos. 3,897,213, 3,920,397, 3,925,019 and 3,926,559.

[0061] The conditions for regeneration are similar to those set forth with respect to the system of Figure 1.

[0062] In order to illustrate the present invention, the following examples of its practice are provided.

Example 1

[0063] This example illustrates the use of an electrolytic chemical packed bed suppressor of the type illustrated in Figure 3. The unit includes a 4x50 mm column. A length of 0.5 mm platinum wire is coiled in a helical spring-like configuration with the outer diameter of the coil about 4 mm and the coil extending approximately the entire length of the suppressor bed. The second electrode is a straight length of 0.5 mm platinum wire extending the entire length of the column coaxial to the coil. Both of the electrodes exit from the coil through fittings that provide liquid tight seal and make contact with the power supply. The electrode separation is about 2 mm.

[0064] The resin was first converted to the exhausted (sodium ion) form with sodium hydroxide, then, with eluent flowing at 2 mL/min, a voltage of 9 volts was applied using the outer coil electrode as the anode. About 500 mA current was obtained, accompanied by visible gassing. The effluent was basic. These observations were compatible with regeneration. The current was applied for 5 minutes, then shut off. Conductivity of the effluent decreased rapidly in the period of about one minute from a reading from about 1000 µS to about 600 µS. This indicated that the hydronium ion had been injected electrochemically into the suppressor bed. A 7-anion standard was run:

Column: AS4A SC
Flow rate: 2 mL/min
Eluent: 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$
Injection volume: 25 µL

2 ppm F^-	15 ppm NO_3^-
3 ppm Cl^-	15 ppm PO_4^{3-}
1 ppm NO_2^-	15 ppm SO_4^{2-}
10 ppm Br^-	

[0065] The suppressor was then regenerated at 500 mA for a further 2 minutes and allowed to equilibrate for about 1 minute after stopping the current. The chromatogram of Figure 7 was obtained illustrating regeneration.

Example 2

[0066] This example illustrates the use of an electrolytic chemical packed bed suppressor of the type illustrated in Figure 5. The unit includes a 6x20 mm column. Porous electrodes were fabricated from platinum mesh and placed at either end of the resin bed. Both of the electrodes were connected to the power supply by wires through fittings in the body of the column that provide a liquid tight seal and make contact with the power supply.

[0067] Dowex 50W-X8 resin was first converted to the exhausted (sodium ion) form with sodium hydroxide. An external source of deionized water was supplied as shown in Figure 2. A voltage of 13 volts was applied from a DC power supply while deionized water was pneumatically pumped through the ion exchange bed at a flow rate of 0.3 mL/minute in the direction from the anode to the cathode (from bottom to top). Thus, sodium hydroxide formed at the cathode was swept from the bed along with the hydrogen and oxygen gases formed at the electrodes. The potential of 13 volts was maintained for 7.5 minutes and the deionized water flow maintained for a further 0.5 minutes. The suppressor was then connected by switching valves 170 and 172 to the exit of the separator column such that the cathode end was attached to the outlet of the separator column and the anode end was attached to the conductivity cell.

[0068] The chromatographic system with eluent flowing was allowed to equilibrate for 2.5 minutes. During this time the conductivity of the effluent dropped from 470 µS to 16 µS. The sample was injected and the chromatogram shown in Figure 8 was obtained.

Column: AS4A SC
Flow rate: 2 mL/min
Eluent: 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$
Injection volume: 20 µL

2 ppm F^-	10 ppm NO_3^-
3 ppm Cl^-	15 ppm PO_4^{3-}
15 ppm SO_4^{2-}	

Claims

1. A method of anion or cation analysis by ion chromatography using periodic electrolytic chemical regeneration of a packed bed suppressor, said method comprising

   (a) chromatographically separating ionic species in a first liquid sample to be detected in a water-containing eluent solution comprising electrolyte to form a first chromatography effluent including separated ionic species,
   (b) flowing said first chromatography effluent through a first packed bed suppressor (162,276) including suppressor ion exchange resin with exchangeable ions to convert said electrolyte to weakly ionized form during suppression, thereby depleting at least some of said exchangeable ions on said suppressor ion exchange resin,
   (c) flowing first suppressor effluent including the separated ionic species from said first packed bed suppressor (162,276) through a detector (166,168,284,286) in which the separated ionic species are detected to form a detector effluent, said method being characterized by
   (d) applying an electrical potential through said first packed resin bed suppressor (162,276) while flowing an aqueous liquid stream therethrough to electrolyze water in said aqueous liquid stream and thereby regenerate the exchangeable ions on said first suppressor ion exchange resin, the application of said electrical potential being discontinued during steps (a), (b) and (c).

2. A method as claimed in claim 1 in which the ionic species are anions and in which in step (d) water in said aqueous liquid in said first packed bed suppressor (162,276) is electrolyzed to generate hydronium ions for regeneration of said exchangeable ions.

3. A method as claimed in claim 1 in which the ionic species are cations and in which in step (d) water in said aqueous liquid in said packed bed suppressor (162,276) is electrolyzed to generate hydroxide ions for regeneration of said exchangeable ions.

4. A method as claimed in any one of claims 1 to 3 further comprising the steps of

   (e) after termination of steps (a), (b) and (c), chromatographically separating a second liquid sample comprising ionic species in an eluent comprising an electrolyte to form a second chromatographic effluent including separated ionic species,
   (f) flowing said second chromatographic effluent through a second packed bed suppressor (266) including suppressor ion exchange resin to convert said electrolyte to weakly ionized form,
   (g) flowing second suppressor effluent from said second packed bed suppressor (266) through said detector (284,286) to detect said separated ionic species and form a detector effluent, and
   (h) flowing said detector effluent through said first packed bed suppressor (276), said detector effluent comprising said aqueous liquid stream in step (d).

5. A method as claimed in claim 4 further comprising, after steps (e), (f), and (g), flowing the detector effluent in step (c) through said second packed bed suppressor ion exchange resin and applying an electrical potential to the same to regenerate the exchangeable ions thereon.

6. A method as claimed in any one of claims 1 to 3 further comprising:

   (e) flowing a water-containing eluent solution comprising electrolyte through a flow-through polishing unit (266) comprising ion exchange resin having exchangeable ions to convert said electrolyte into weakly ionized form and to form a polished liquid effluent, and
   (f) flowing said polished liquid effluent through said first packed bed suppressor (276) during step (d), said polished effluent comprising said aqueous liquid stream.

7. A method as claimed in claim 6 further comprising the steps of

   (g) regenerating the ion exchange resin in said polishing unit (266) by flowing the effluent from said detector (284,286) in step (c) through said polishing unit (266) and applying an electrical potential through said polishing unit ion exchange resin to regenerate the exchangeable ions thereon.

8. A method as claimed in any one of claims 1 to 7 in which said aqueous liquid stream comprises a water-containing eluent solution.

9. A method as claimed in any one of claims 1 to 7 in which said aqueous liquid stream is supplied from a source of water independent of said eluent solution.

10. A method as claimed in claim 9 in which said water is deionized water.

11. An apparatus for analysis of ions in a liquid sample solution, said apparatus comprising

(a) a first reservoir for a water-containing eluent solution comprising electrolyte,
(b) chromatographic separating means (158,258) in communication with said first reservoir for receiving eluent therefrom, said chromatographic separating means (158,258) comprising a chromatographic separating medium adapted to separate ionic species of a sample eluted therethrough using said eluent solution,
(c) means (150,250) for injecting a liquid sample into said chromatographic separation means (158,258),
(d) a first suppressor (162,276) comprising an ion exchange resin bed in communication with said chromatographic separating means (158,258),
(e) a detector (166,168,284,286) in communication with said first suppressor (162,276), said apparatus being characterized in that it further comprises
(f) means (164,272) for applying an electrical potential through said ion exchange resin bed of said first suppressor (162, 276), whereby, in use, water in a flowing aqueous stream is electrolysed and said ion exchange resin of said first suppressor (162, 276) is regenerated.

12. An apparatus as claimed in claim 11 in which said chromatographic separating means (258) includes an outlet for said separated sample, said first suppressor (276) has an inlet and an outlet, said inlet being in communication with the outlet of said chromatographic separating means (258), and in which said detector (284,286) is in communication with the outlet of said first suppressor (276), the apparatus further comprising

(g) a second suppressor (266) comprising an ion exchange resin bed in communication with said detector (284,286),
(h) means (272) for applying an electrical potential through said ion exchange resin bed of said second suppressor (266), and
(i) valve means (262,270) including a first and second valve position, said first valve position permitting liquid flow from said eluent reservoir, through said chromatographic separation means (258), said ion exchange resin bed of said first suppressor (276), said detector (284,286), and said ion exchange resin bed of said second suppressor (266) and said second position permitting liquid flow from said eluent reservoir, through said ion exchange resin bed of said second suppressor (266), said detector (284,286), and said ion exchange resin bed of said first suppressor (276), whereby, in use, in said first valve position, the ions in a sample solution are separated in said chromatographic separating means (258) and carried in said eluent through said ion exchange resin bed of said first suppressor (276) in which said electrolyte is converted to weakly ionized form during suppression, through said detector (284,286) in which ions are detected and through said ion exchange resin bed of said second suppressor (266), and in said second valve position, the eluent solution flows at least through said ion exchange resin bed of said second suppressor (266), and said ion exchange resin bed of said first suppressor (276), and said applying means (272) being capable of applying said electrical potential across said ion exchange resin bed of said first suppressor (276) to regenerate the same with said valve means in said second valve position.

13. An apparatus as claimed in claim 12 in which, in use, with said valve means in said second valve position, the eluent flows from said eluent reservoir through said chromatographic separating means (258) to said ion exchange resin bed of said second suppressor (266).

14. An apparatus as claimed in claim 12 in which said applying means (272) is capable of applying said electrical potential across said ion exchange resin bed of said second suppressor (266) with said valve means in said first valve position.

15. An apparatus as claimed in claim 11 further comprising

(g) a second reservoir (176) for containing water which is in communication with said first suppressor (162),
(h) valve means (170,172) including a first and second valve position, said first valve position permitting liquid flow from said first reservoir, through said chromatographic separation means (158), said ion exchange resin bed of said first suppressor (162), and said detector (166,168), and said second position permitting liquid flow from said second reservoir (176), through said ion exchange resin bed of said first suppressor (162), whereby, in use, in said first valve position, the ions in a sample solution are separated in said chromatographic separating means (158) and carried in said eluent through said ion exchange resin bed of said first suppressor (162) in which said electrolyte is converted to weakly dissociated form during suppression, and through said detector (166,168) in which the ions are detected, and in said sec-

ond valve position, water from said second reservoir (176) flows at least through said ion exchange resin bed of said first suppressor (162), said applying means (164) being capable of applying said electrical potential across said ion exchange resin bed of said first suppressor (162) to regenerate the same with said valve means in said second valve position.

16. A suppressor for use in an apparatus for analysis of ions in a liquid sample solution, said suppressor comprising a flow-through housing (200,202), a suppressor ion exchange resin bed (220) disposed in said housing (200,202), and means (214,216,218) for applying an electrical potential through said suppressor ion exchange resin bed (220), whereby, in use, water in a flowing aqueous stream is electrolyzed and said suppressor ion exchange resin (220) is regenerated after use to suppress electrolyte in an eluent stream.

Patentansprüche

1. Anionen- oder Kationenanalyseverfahren durch Ionenchromatographie unter Verwendung einer periodischen elektrolytischen chemischen Regeneration eines Füllstoffbett-Suppressors, bei welchem

   a) chromatographisch Ionenarten in einer ersten Flüssigkeitsprobe, die in einer Wasser enthaltenden Eluatlösung mit Elektrolyt nachzuweisen sind, zur Bildung eines ersten Chromatographie-Abstroms, der getrennte Ionenarten aufweist, getrennt werden
   b) der erste Chromatographie-Abstrom durch einen ersten Füllstoffbett-Suppressor (162, 276) strömen gelassen wird, der ein Ionenaustauschharz mit austauschbaren Ionen aufweist, um den Elektrolyt in eine schwach ionisierte Form während der Suppression umzuwandeln, wodurch wenigstens einige der austauschbaren Ionen an dem Suppressor-Ionenaustauschharz entzogen werden, und
   c) der erste Suppressor-Abstrom mit den getrennten Ionenarten aus dem ersten Füllstoffbett-Suppressor (162, 276) durch einen Detektor (166, 168, 284, 286) strömen gelassen wird, in welchem die abgetrennten Ionenarten nachgewiesen werden und ein Detektorabstrom gebildet wird,

   dadurch gekennzeichnet,
   d) daß an den ersten Harz-Füllstoffbett-Suppressor (162, 276) eine elektrische Spannung angelegt wird, während durch ihn hindurch ein wasserhaltiger Flüssigkeitsstrom strömen gelassen wird, um das Wasser in dem wasserhaltigen Flüssigkeitsstrom zu elektrolysieren und um dadurch die austauschbaren Ionen an dem ersten Suppressor-Ionenaustauschharz zu regenerieren, wobei das Anlegen der elektrischen Spannung während der Schritte a), b) und c) unterbrochen wird.

2. Verfahren nach Anspruch 1, bei welchem die Ionenarten Anionen sind und bei welchem im Schritt (d) Wasser in der wasserhaltigen Flüssigkeit in dem ersten Füllstoffbett-Suppressor (162, 276) elektrolysiert wird, um Hydroniumionen zur Regeneration der austauschbaren Ionen zu erzeugen.

3. Verfahren nach Anspruch 1, bei welchem die Ionenarten Kationen sind und bei welchem im Schritt (d) Wasser in der wasserhaltigen Flüssigkeit in dem Füllstoffbett-Suppressor (162, 276) elektrolysiert wird, um Hydroxydionen für die Regeneration der austauschbaren Ionen zu erzeugen.

4. Verfahren nach einem der Ansprüche 1 bis 3, welches weiterhin die Schritte aufweist,

   e) nach Beendigung der Schritte (a), (b) und (c) eine zweite Flüssigkeitsprobe chromatographisch abzutrennen, die Ionenarten in einem Eluat mit einem Elektrolyten aufweist, um einen zweiten chromatographischen Abstrom mit den abgetrennten Ionenarten zu bilden,
   f) den zweiten chromatographischen Abstrom durch einen zweiten Füllstoffbett-Suppressor (266) mit einem Suppressor-Ionenaustauschharz strömen zu lassen, um den Elektrolyten in eine schwach ionisierte Form umzuwandeln,
   g) den zweiten Suppressorabstrom aus dem zweiten Füllstoffbett-Suppressor (266) durch den Detektor (284, 286) strömen zu lassen, um die abgetrennten Ionenarten nachzuweisen und um einen Detektorabstrom zu bilden, und
   h) den Detektorabstrom durch den ersten Füllstoffbett-Suppressor (276) strömen zu lassen, wobei der Detektorabstrom den wasserhaltigen Flüssigkeitsstrom in dem Schritt (d) umfaßt.

5. Verfahren nach Anspruch 4, bei welchem weiterhin nach den Schritten (e), (f) und (g) der Detektorabstrom in Schritt (c) durch das Ionenaustauschharz des zweiten Füllstoffbett-Suppressors strömen gelassen wird und eine elektrische Spannung an dieses zur Regenerierung der austauschbaren Ionen daran angelegt wird.

6. Verfahren nach einem der Ansprüche 1 bis 3, bei welchem weiterhin

   e) eine wasserenthaltende Eluatlösung mit Elektrolyt durch eine Durchfluß-Feinstreini-

gungseinheit (266) strömen gelassen wird, die ein Ionenaustauschharz mit austauschbaren Ionen aufweist, um den Elektrolyten in eine schwach ionisierte Form umzuwandeln und um einen feinstgereinigten Flüssigkeitsabstrom zu bilden, und
f) der feinstgereinigte Flüssigkeitsabstrom während Schritt (d) durch den ersten Füllstoffbett-Suppressor (276) strömen gelassen wird, wobei der feinstgereinigte Abstrom den wasserhaltigen Flüssigkeitsstrom aufweist.

7. Verfahren nach Anspruch 6, welches weiterhin die Schritte aufweist,
g) das Ionenaustauschharz in der Feinstreinigungseinheit (266) dadurch zu regenerieren, daß der Abstrom aus dem Detektor (284, 286) in Schritt (c) durch die Feinstreinigungseinheit (266) strömen gelassen wird und eine elektrische Spannung an das Feinstreinigungseinheits-Ionenaustauschharz angelegt wird, um die austauschbaren Ionen daran zu regenerieren.

8. Verfahren nach einem der Ansprüche 1 bis 7, bei welchem der wasserhaltige Flüssigkeitsstrom eine Wasser enthaltende Eluatlösung aufweist.

9. Verfahren nach einem der Ansprüche 1 bis 7, bei welchem der wasserhaltige Flüssigkeitsstrom unabhängig von dem Eluatstrom von einer Wasserquelle zugeführt wird.

10. Verfahren nach Anspruch 9, bei welchem das Wasser entionisiertes Wasser ist.

11. Vorrichtung zur Analyse von Ionen in einer Flüssigkeitsprobenlösung

a) mit einem ersten Speicher für eine Wasser enthaltende Eluatlösung, die einen Elektrolyten aufweist,
b) mit einer chromatographischen Trenneinrichtung (158, 258) in Verbindung mit dem ersten Speicher für die Aufnahme von Eluat aus ihm, wobei die chromatographische Trenneinrichtung (158, 258) ein chromatographisches Trennmedium aufweist, das zum Abtrennen von Ionenarten einer durch es hindurch eluierten Probe bei Verwendung der Eluatlösung geeignet ist,
c) mit einer Einrichtung (150, 250) zum Einspritzen einer Flüssigkeitsprobe in die chromatographische Trenneinrichtung (158, 258),
d) mit einem ersten Suppressor (162, 276), der ein Ionenaustauschharzbett aufweist, das in Verbindung mit der chromatographischen Trenneinrichtung (158, 258) steht, und
e) mit einem Detektor (166, 168, 284, 286), der in Verbindung mit dem ersten Suppressor (162, 276) steht,

gekennzeichnet weiterhin durch,
f) eine Einrichtung (164, 272) zum Anlegen einer elektrischen Spannung an das Ionenaustauschharzbett des ersten Suppressors (162, 276), wodurch im Einsatz Wasser in einem fließenden wasserhaltigen Strom elektrolysiert und das Ionenaustauschharz des ersten Suppressors (162, 276) regeneriert wird.

12. Vorrichtung nach Anspruch 11, bei welcher die chromatographische Trenneinrichtung (258) einen Auslaß für die abgetrennte Probe aufweist, der erste Suppressor (276) einen Einlaß und einen Auslaß hat, der Einlaß in Verbindung mit dem Auslaß der chromatographischen Trenneinrichtung steht, und der Detektor (284, 286) in Verbindung mit dem Auslaß des ersten Suppressors (276) steht, wobei die Vorrichtung weiterhin

g) einen zweiten Suppressor (266), welcher ein Ionenaustauschharzbett aufweist, das in Verbindung mit dem Detektor (284, 286) steht,
h) eine Einrichtung (272) zum Anlegen einer elektrischen Spannung an das Ionenaustauschharzbett des zweiten Suppressors (266) und
i) eine Ventileinrichtung (262, 270) mit einer ersten und einer zweiten Ventilstellung aufweist,

- wobei die erste Ventilstellung ermöglicht, daß Flüssigkeit aus dem Eluatspeicher durch die chromatographische Trenneinrichtung (258), das Ionenaustauschharzbett des ersten Suppressors (276), den Detektor (284, 286) und das Ionenaustauschharzbett des zweiten Suppressors (266) strömt, und
- die zweite Stellung einen Flüssigkeitsstrom aus dem Eluatspeicher durch das Ionenaustauschharzbett des zweiten Suppressors (266), den Detektor (284, 286) und das Ionenaustauschharzbett des ersten Suppressors (276) ermöglicht,
- wodurch im Einsatz in der ersten Ventilstellung die Ionen einer Probenlösung in der chromatographischen Trenneinrichtung (258) abgetrennt und in dem Eluat durch das Ionenaustauschharzbett des ersten Suppressors (276), in welchem der Elektrolyt während der Suppression in eine schwach ionisierte Form umgewandelt wird, durch den Detektor (284, 286), in dem Ionen nachgewiesen werden, und durch das Ionenaustauschharzbett des zweiten Suppressors (266) transportiert werden,

- wobei in der zweiten Ventilstellung die Eluatlösung wenigstens durch das Ionenaustauschharzbett des zweiten Suppressors (266) und das Ionenaustauschharzbett des ersten Suppressors (276) strömt, und
- wobei die Anlegeeinrichtung (272) in der Lage ist, die elektrische Spannung an das Ionenaustauschharzbett des ersten Suppressors (276) anzulegen, um dieses zu regenerieren, wenn sich die Ventileinrichtung in der zweiten Ventilstellung befindet.

13. Vorrichtung nach Anspruch 12, bei welcher im Einsatz, wenn sich die Ventileinrichtung in der zweiten Ventilstellung befindet, das Eluat aus dem Eluatspeicher durch die chromatographische Trenneinrichtung (258) zu dem Ionenaustauschharzbett des zweiten Suppressors (266) strömt.

14. Vorrichtung nach Anspruch 12, bei welchem die Anlegeeinrichtung (272) in der Lage ist, die elektrische Spannung an das Ionenaustauschharzbett des zweiten Suppressors (266) anzulegen, wenn sich die Ventileinrichtung in der ersten Ventilstellung befindet.

15. Vorrichtung nach Anspruch 11, welche weiterhin

g) einen zweiten wasserenthaltenden Speicher (176), der in Verbindung mit dem ersten Suppressor (162) steht und
h) eine Ventileinrichtung (170, 172) mit einer ersten und einer zweiten Ventilstellung aufweist,

- wobei die erste Ventilstellung einen Flüssigkeitsstrom aus dem ersten Speicher durch die chromatographische Trenneinrichtung (158), das Ionenaustauschharzbett des ersten Suppressors (162) und den Detektor (166, 168) ermöglicht,
- wobei die zweite Stellung einen Flüssigkeitsstrom aus dem zweiten Speicher (176) durch das Ionenaustauschharzbett des ersten Suppressors (162) ermöglicht,
- wodurch im Einsatz in der ersten Ventilstellung die Ionen in einer Probenlösung in der chromatographischen Trenneinrichtung (158) abgetrennt und in dem Eluat durch das Ionenaustauschharzbett des ersten Suppressors (162), in welchem der Elektrolyt in eine schwach dissoziierte Form während der Suppression umgewandelt wird, und durch den Detektor (166, 168) transportiert wird, in welchem die Ionen nachgewiesen werden,
- wobei in der zweiten Ventilstellung Wasser aus dem zweiten Speicher (176) wenigstens durch das Ionenaustauschharzbett des ersten Suppressors (162) strömt, und
- wobei die Anlegeeinrichtung (164) in der Lage ist, die elektrische Spannung an das Ionenaustauschharzbett des ersten Suppressors (162) anzulegen, um dieses zu regenerieren, wenn sich die Ventileinrichtungen in der zweiten Ventilstellung befinden.

16. Suppressor zur Verwendung in einer Vorrichtung zur Analyse von Ionen in einer Flüssigkeitsprobenlösung, wobei der Suppressor ein Durchflußgehäuse (200, 202), ein Suppressor-Ionenaustauschharzbett (220), das in dem Gehäuse (200, 202) angeordnet ist, und eine Einrichtung (214, 216, 218) zum Anlegen einer elektrischen Spannung an das Suppressor-Ionenaustauschharzbett (220) aufweist, wodurch im Einsatz Wasser in einem fließenden wasserhaltigen Strom elektrolysiert wird und das Suppressor-Ionenaustauschharz (220) nach Verwendung regeneriert wird, um Elektrolyten in einem Eluatstrom einer Suppression zu unterwerfen.

Revendications

1. Procédé d'analyse d'anions ou de cations par chromatographie ionique utilisant la régénération chimique électrolytique périodique d'un extracteur à lit tassé, ce procédé comprenant

(a) le fait de séparer chromatographiquement des espèces ioniques présentes dans un premier échantillon de liquide à détecter dans une solution d'éluant contenant de l'eau comprenant un électrolyte pour former un premier effluent de chromatographie contenant les espèces ioniques séparées,
(b) faire écouler ce premier effluent de chromatographie à travers un premier extracteur à lit tassé (162, 276) contenant une résine échangeuse d'ions d'extracteur avec des ions échangeables pour amener cet électrolyte sous une forme faiblement ionisée au cours de l'extraction, épuisant ainsi au moins une partie de ces ions échangeables sur cette résine échangeuse d'ions de l'extracteur,
(c) faire écouler un premier effluent d'extracteur contenant les espèces ioniques séparées de ce premier extracteur à lit tassé (162, 276) à travers un détecteur (166, 168, 284, 286) dans lequel les espèces ioniques séparées sont détectées pour former un effluent de détecteur, ce procédé étant caractérisé en ce que
(d) on applique un potentiel électrique à travers ce premier extracteur à lit tassé (162, 276) tout en faisant écouler un courant de liquide aqueux

à travers celui-ci pour électrolyser l'eau dans ce courant de liquide aqueux et régénérer ainsi les ions échangeables sur cette première résine échangeuse d'ions d'extracteur, l'application de ce potentiel électrique étant interrompue au cours des étapes (a), (b) et (c).

2. Procédé selon la revendication 1, dans lequel les espèces ioniques sont des anions et dans lequel, dans l'étape (d), on électrolyse d'abord l'eau de ce liquide aqueux dans ce premier extracteur à lit tassé (162, 276) pour produire des ions hydronium pour la régénération de ces ions échangeables.

3. Procédé selon la revendication 1, dans lequel les espèces ioniques sont des cations et dans lequel, dans l'étape (d), on électrolyse l'eau de ce liquide aqueux présent dans cet extracteur à lit tassé (162, 276) pour produire des ions hydroxyde pour la régénération de ces ions échangeables.

4. Procédé selon l'une quelconque des revendications 1 à 3 comprenant en outre les étapes consistant à

(e) après avoir terminé les étapes (a), (b) et (c), séparer chromatographiquement un second échantillon de liquide comprenant des espèces ioniques dans un éluant comprenant un électrolyte pour former un second effluent chromatographique contenant des espèces ioniques séparées,
(f) faire écouler ce second effluent chromatographique à travers un second extracteur à lit tassé (266) contenant une résine échangeuse d'ions d'extracteur pour amener cet électrolyte en une forme faiblement ionisée,
(g) faire écouler ce second effluent d'extracteur de ce second extracteur à lit tassé (266) à travers ce détecteur (284, 286) pour détecter ces espèces ioniques séparées et former un effluent de détecteur, et
(h) faire écouler cet effluent de détecteur à travers ce premier extracteur à lit tassé (276), cet effluent de détecteur contenant ce courant de liquide aqueux de l'étape (d).

5. Procédé selon la revendication 4, comprenant en outre, après les étapes (e), (f) et (g), le fait de faire écouler l'effluent de l'extracteur de l'étape (c) à travers cette seconde résine échangeuse d'ions d'extracteur à lit tassé et d'appliquer un potentiel électrique à celle-ci pour régénérer les ions échangeables sur celle-ci.

6. Procédé selon l'une quelconque des revendications 1 à 3 comprenant en outre

(e) le fait de faire écouler une solution d'éluant contenant de l'eau comprenant un électrolyte à travers une installation d'adoucissage à écoulement continu (266) comprenant une résine échangeuse d'ions ayant des ions échangeables pour amener cet électrolyte sous une forme faiblement ionisée et pour former un effluent liquide adouci, et
(f) faire écouler cet effluent liquide adouci à travers ce premier extracteur à lit tassé (276) au cours de l'étape (d), cet effluent adouci comprenant ce courant liquide aqueux.

7. Procédé selon la revendication 6, comprenant en outre les étapes consistant à

(g) régénérer la résine échangeuse d'ions de cette installation de polissage (266) en faisant écouler l'effluent de ce détecteur (284, 286) de l'étape (c) à travers cette installation d'adoucissage (266) et appliquer un potentiel électrique à travers cette résine échangeuse d'ions de l'installation d'adoucissage pour régénérer les ions échangeables sur celle-ci.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel ce courant de liquide aqueux comprend une solution d'éluant contenant de l'eau.

9. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel ce courant de liquide aqueux est fourni par une source d'eau indépendante de cette solution d'éluant.

10. Procédé selon la revendication 9, dans lequel cette eau est de l'eau désionisée.

11. Appareil pour l'analyse des ions dans une solution d'échantillon liquide, cet appareil comprenant

(a) un premier réservoir pour une solution d'éluant contenant de l'eau comprenant un électrolyte,
(b) des moyens de séparation chromatographique (158, 258) en communication avec ce premier réservoir pour recevoir l'éluant de celui-ci, ces moyens de séparation chromatographique (158, 258) comprenant un milieu de séparation chromatographique conçu pour séparer des espèces ioniques contenues dans un échantillon élué à travers celui-ci en utilisant cette solution d'éluant,
(c) des moyens (150, 250) pour injecter un échantillon de liquide dans ces moyens de séparation chromatographiques (158, 258),
(d) un premier extracteur (162, 276) comprenant un lit de résine échangeuse d'ions en communication avec ces moyens de séparation chromatographique (158, 258),
(e) un détecteur (166, 168, 284, 286) en com-

munication avec ce premier extracteur (162, 276), cet appareil étant caractérisé en ce qu'il comprend en outre

(f) des moyens (164, 272) pour appliquer un potentiel électrique à travers ce lit de résine échangeuse d'ions de ce premier extracteur (162, 276), grâce à quoi, lors de l'utilisation, l'eau présente dans un courant aqueux s'écoulant est électrolysée et cette résine échangeuse d'ions de ce premier extracteur (162, 276) est régénérée.

12. Appareil selon la revendication 11, dans lequel ce moyen de séparation chromatographique (258) contient un orifice de sortie pour cet échantillon séparé, ce premier extracteur (276) a un orifice d'entrée et un orifice de sortie, cet orifice d'entrée étant en communication avec l'orifice de sortie de ce moyen de séparation chromatographique (258), et dans lequel ce détecteur (284, 286) est en communication avec l'orifice de sortie de ce premier extracteur (276), l'appareil comprenant en outre

(g) un second extracteur (266) comprenant un lit de résine échangeuse d'ions en communication avec ce détecteur (284, 286),
(h) des moyens (272) pour appliquer un potentiel électrique à travers ce lit de résine échangeuse d'ions de ce second extracteur (266), et
(i) des moyens de soupape (262, 270) contenant une première et une seconde position de la soupape, cette première position de la soupape permettant un courant de liquide provenant de ce réservoir d'éluant, à travers ce moyen de séparation chromatographique (258), ce lit de résine échangeuse d'ions de ce premier extracteur (276), ce détecteur (284, 286) et ce lit de résine échangeuse d'ions de ce second extracteur (266) et cette seconde position permettant au courant de liquide provenant de ce réservoir d'éluant, à travers ce lit de résine échangeuse d'ions de ce second extracteur (266), ce détecteur (284, 286) et ce lit de résine échangeuse d'ions de ce premier extracteur (276), grâce à quoi, lors de l'utilisation, dans cette première position de la soupape, les ions présents dans une solution d'échantillon sont séparés dans ce moyen de séparation chromatographique (258) et transportés dans cet éluant à travers ce lit de résine échangeuse d'ions de ce premier extracteur (276) dans lequel cet électrolyte est amené sous une forme faiblement ionisée au cours de l'extraction, à travers ce détecteur (284, 286) dans lequel ces ions sont détectés et à travers ce lit de résine échangeuse d'ions de ce second extracteur (266) et dans cette seconde position de la soupape, la solution d'éluant s'écoule au moins à travers ce lit de résine échangeuse d'ions de ce second extracteur (266), et ce lit de résine échangeuse d'ions de ce premier extracteur (276), et ce moyen d'application (272) étant capable d'appliquer ce potentiel électrique à travers ce lit de résine échangeuse d'ions de ce premier extracteur (276) pour régénérer celui-ci avec ce moyen de soupape dans cette seconde position de la soupape.

13. Appareil selon la revendication 12, dans lequel, lors de l'utilisation, avec ce moyen de soupape dans cette seconde position de la soupape, l'éluant s'écoule de ce réservoir d'éluant à travers ce moyen de séparation chromatographique (258) vers ce lit de résine échangeuse d'ions de ce second extracteur (266).

14. Appareil selon la revendication 12, dans lequel ce moyen d'application (272) est capable d'appliquer ce potentiel électrique à travers ce lit de résine échangeuse d'ions de ce second extracteur (266) avec ce moyen de soupape dans cette première position de soupape.

15. Appareil selon la revendication 11, comprenant en outre

(g) un second réservoir (176) pour contenir de l'eau qui est en communication avec ce premier extracteur (162),
(h) un moyen de soupape (170, 172) contenant une première et une seconde positions de la soupape, cette première position de la soupape permettant au liquide de s'écouler de ce premier réservoir, à travers ce moyen de séparation chromatographique (158), ce lit de résine échangeuse d'ions de ce premier extracteur (162) et ce détecteur (166, 168), et cette seconde position permettant au cours de liquide de s'écouler de ce second réservoir (176), à travers ce lit de résine échangeuse d'ions de ce premier extracteur (162), grâce à quoi, lors de l'utilisation, dans cette première position de la soupape, les ions d'une solution d'échantillon sont séparés dans ce moyen de séparation chromatographique (158) et transportés dans cet éluant à travers ce lit de résine échangeuse d'ions de ce premier extracteur (162) dans lequel cet électrolyte est amené sous une forme faiblement dissociée au cours de l'extraction, et à travers ce détecteur (166, 168) dans lequel les ions sont détectés, et dans cette seconde position de soupape, l'eau provenant de ce second réservoir (176) s'écoule au moins à travers ce lit de résine échangeuse d'ions de ce premier extracteur (162), ce moyen d'application (164) étant capable d'appliquer ce potentiel

électrique à travers ce lit de résine échangeuse d'ions de ce premier extracteur (162) pour régénérer celui-ci avec ce moyen de soupape dans cette seconde position de la soupape.

16. Extracteur pour l'utilisation dans un appareil pour l'analyse d'ions dans une solution d'échantillon liquide, cet extracteur comprenant un boîtier d'écoulement (200, 202), un lit de résine échangeuse d'ions de l'extracteur (220) disposé dans ce boîtier (200, 202), et des moyens (214, 216, 218) pour appliquer un potentiel électrique à travers ce lit de résine échangeuse d'ions de l'extracteur (220), grâce à quoi, lors de l'utilisation, l'eau présente dans un courant aqueux s'écoulant est électrolysée et cette résine échangeuse d'ions de l'extracteur (220) est régénérée après utilisation pour supprimer l'électrolyte dans un courant d'éluant.

Figure 1

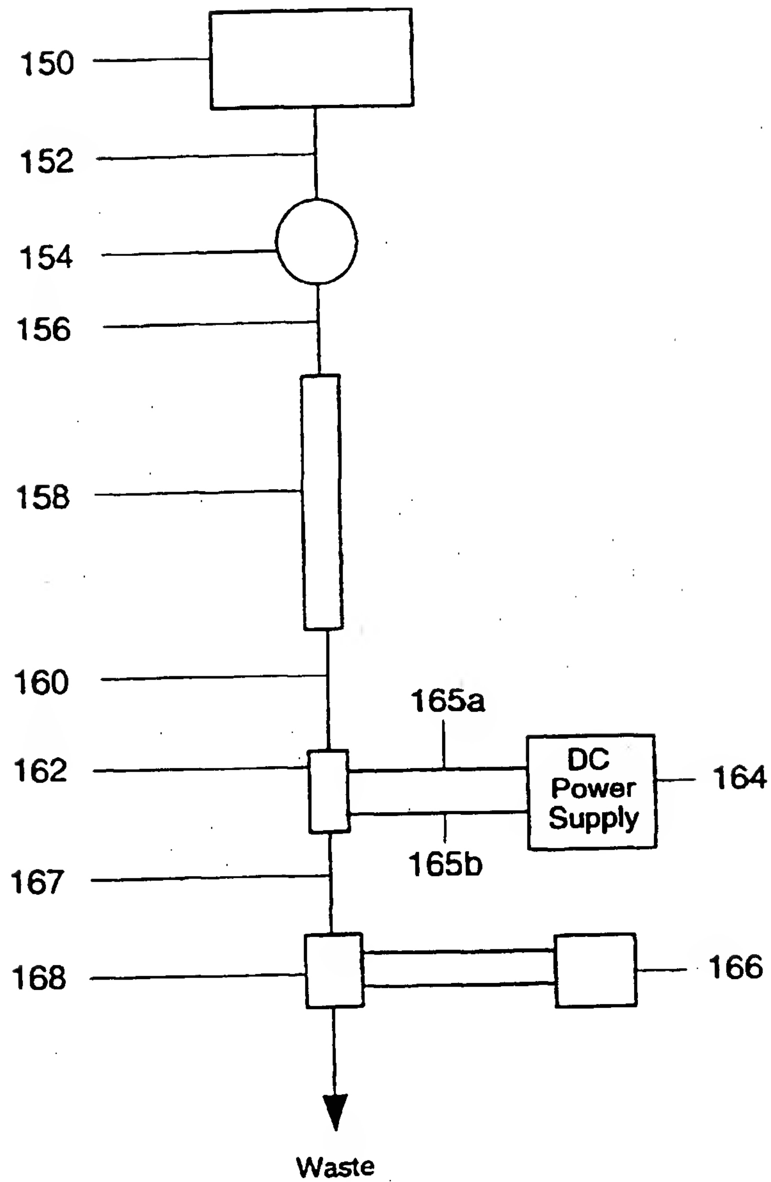

150
152
154
156
158
160
165a
162
DC
Power
Supply
164
165b
167
168
166
Waste

Figure 2

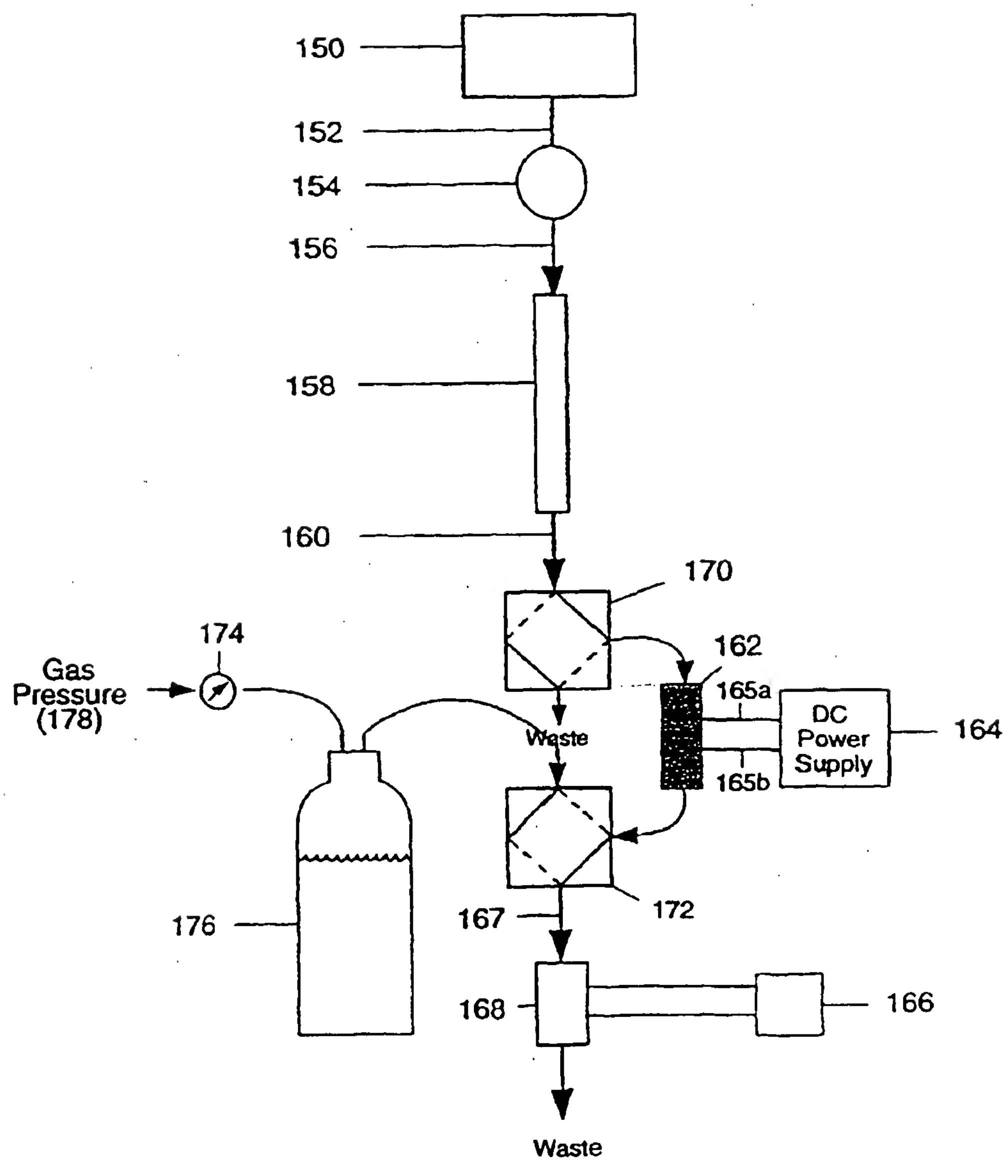

150
152
154
156
158
160
170
162
174
Gas Pressure (178)
165a
DC Power Supply
164
Waste
165b
176
167
172
168
166
Waste

Figure 3

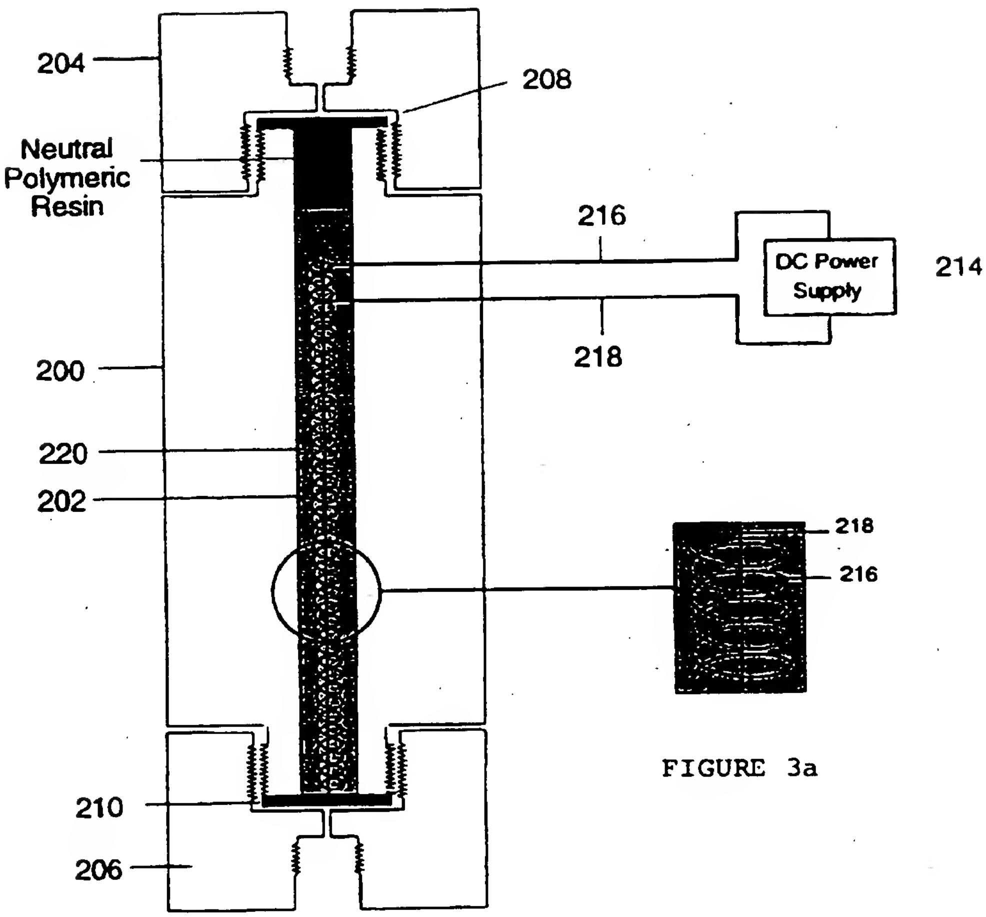
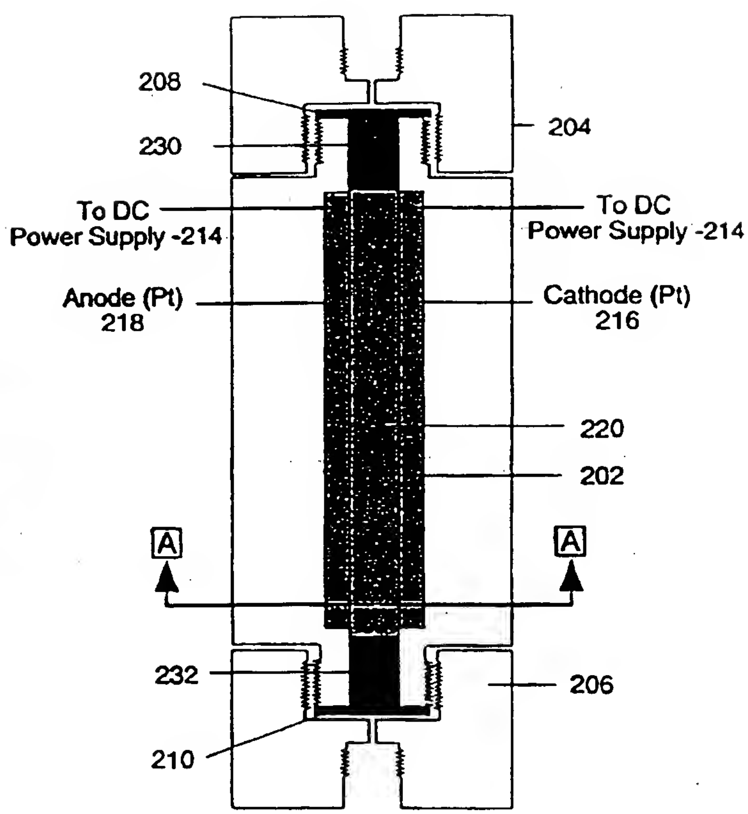


FIGURE 3a

Figure 4



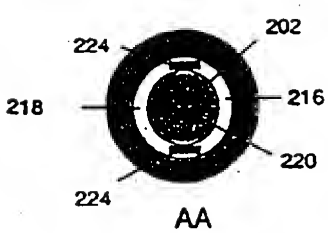


FIGURE 4a

Figure 5

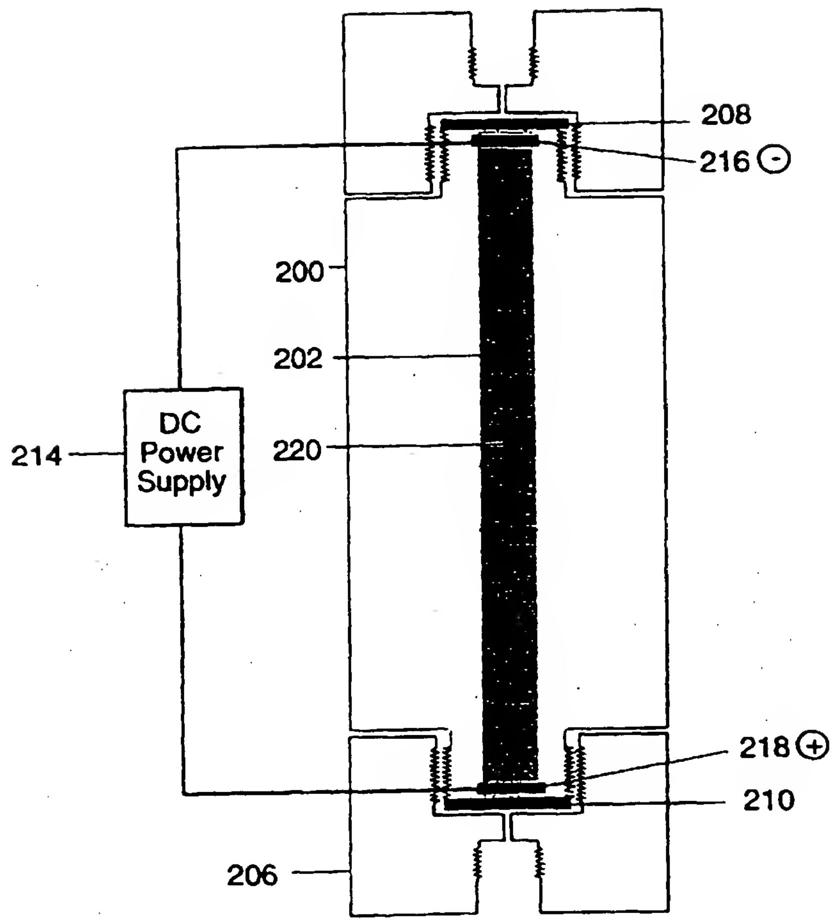


Figure 6

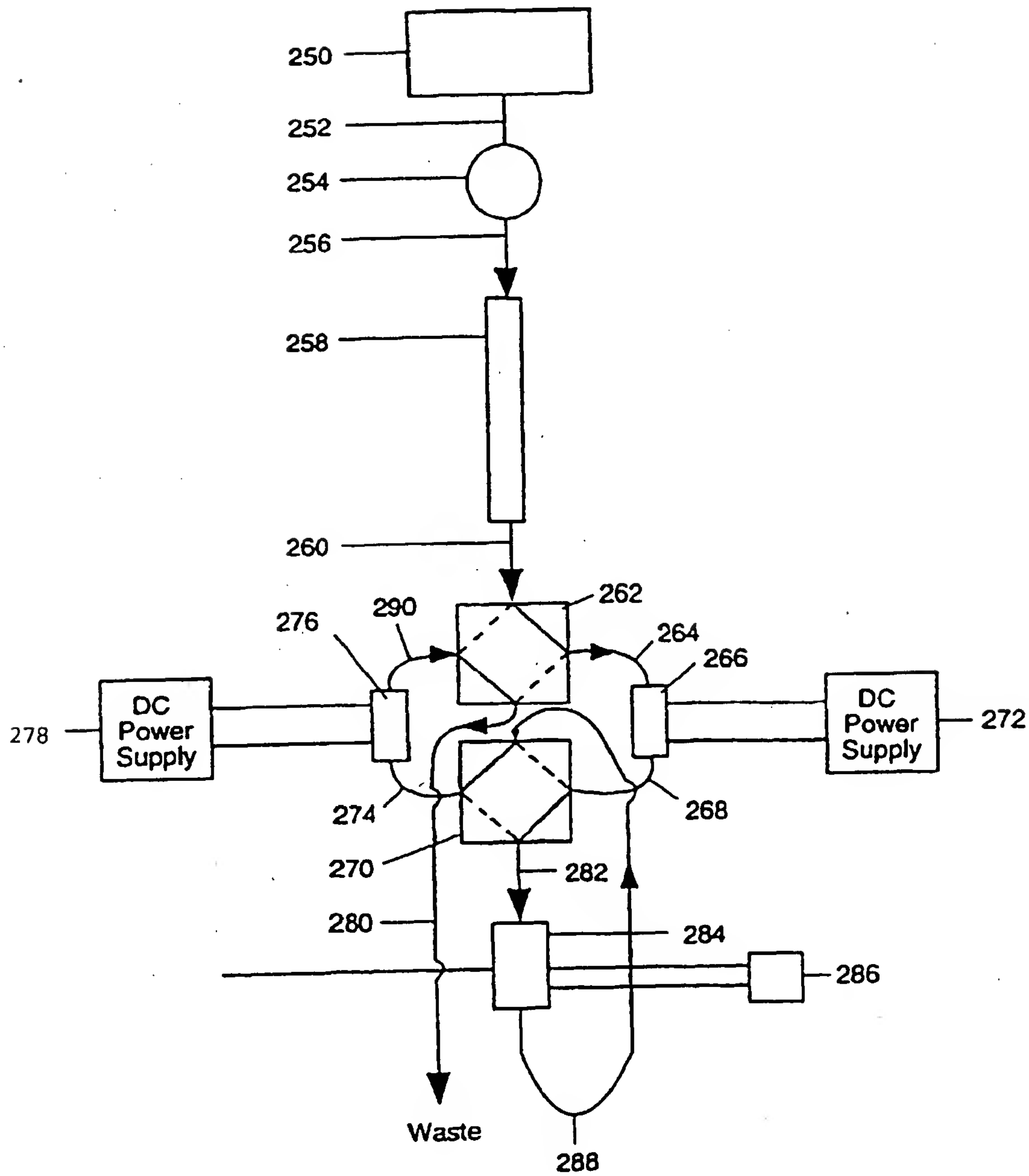

250
252
254
256
258
260
262
290
276
264
266
DC Power Supply
278
DC Power Supply
272
274
268
270
282
280
284
286
Waste
288

Figure 7

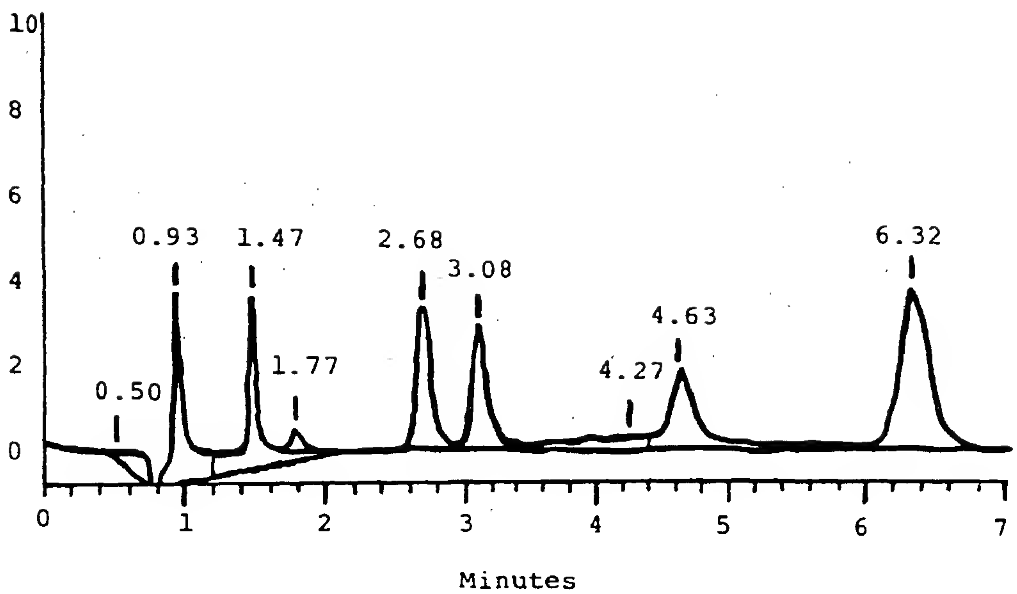


Figure 8